THIN FILM $CuInS_2$ PREPARED BY SPRAY PYROLYSIS WITH SINGLE-SOURCE PRECURSORS

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ABSTRACT

Both horizontal hot-wall and vertical cold-wall atmospheric chemical spray pyrolysis processes deposited near single-phase stoichiometric $CuInS_2$ thin films. Single-source precursors developed for ternary chalcopyrite materials were used for this study, and a new liquid phase single-source precursor was tested with a vertical cold-wall reactor. The depositions were carried out under an argon atmosphere, and the substrate temperature was kept at 400 °C. Columnar grain structure was obtained with vapor deposition, and the granular structure was obtained with (liquid) droplet deposition. Conductive films were deposited with planar electrical resistivities ranging from 1 to 30 Ω •cm.

INTRODUCTION

Photovoltaic power is an important power source for both off-grid terrestrial and extraterrestrial use. Thin film polycrystalline materials have been studied extensively for solar cell applications because their performance is typically better than amorphous thin film materials and their production cost is less than that of bulk-based single-crystalline materials [1]. Furthermore, their polycrystalline nature allows their formation on many different types of substrates including glass, metal foil, and lightweight flexible polymer substrates. Using polymer substrates will particularly benefit space missions by reducing the payload of spacecraft. However, existing polymer substrates can be processed only under limited preparative conditions because of their poor thermal stability. Consequently, the substrate temperature at which the desired materials can be formed is the most critical process parameter, and the decomposition temperature of the precursor should be low enough to facilitate the process with polymer substrates.

Chemical vapor deposition (CVD) is one of the most widely used thin film deposition methods. A chemical precursor for CVD is typically either a gas or condensed phase with a high vapor pressure. However precursors that decompose at low temperatures often have a low vapor pressure, and it is not straightforward to minimize their thermal degradation when precursor temperature is additionally increased to achieve a vapor pressure high enough to deliver them. Delivering the precursor as an aerosol is one of the most convenient methods to resolve this issue because there is no additional heating involved. However, it is important to point out that thin film formation via aerosol processing is complicated by many different phenomena caused by the complex dynamics of aerosol evaporation, precursor decomposition, and gas phase condensation.

For either the CVD or spray pyrolysis, it is more convenient to use a single-source precursor because it simplifies the process and typically provides a safer route to process materials. More facile control of the stoichiometry is another potential advantage. The National Aeronautics and Space Administration (NASA) has been interested in developing low-temperature solar cells for future missions and we have demonstrated the synthesis of new single-source precursors for thin film $CuInS_2$ materials [2, 3]. Their thermal properties may allow utilization of lightweight polymer substrates for solar cell arrays. Along with Cu(In,Ga)Se2, which is currently used for the most efficient thin film solar cells, $CuInS_2$ is a promising absorber material for the solar cells due to its optimum energy band gap.

In this study, $CuInS_2$ thin films were deposited using a liquid single-source precursor in a vertical cold-wall aerosol reactor for the first time. Furthermore, NASA's ongoing effort to create better single-source precursors and to understand the aerosol processing of the materials finding out the optimal route for processing is reported.

EXPERIMENTAL

For this study, both $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$ and $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ as a solid and a liquid single-source precursors, were respectively prepared for the aerosol process. A modified version of the procedure reported by Kanatzidis [4] was used to synthesize the single-source precursors. The difference is that the thiol derivative was generated in situ by reaction of the conjugate acid with NaOEt in methanol producing no undesirable side products in addition to an 'activated' NaSEt. Detailed studies on the thermal properties of the precursors were reported elsewhere [2, 3]. Because of their sensitivity to oxygen and moisture, the materials were handled in argon filled glove box. Precursors were dis-

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solved in toluene, which was dried and distilled under argon prior to use. The solution concentration was typically 0.01 M.

Spray pyrolysis was performed with both a horizontal hot-wall and a vertical cold-wall reactors. The aerosol was generated by a 2.5 MHz plate nebulizer and a 120 kHz atomizing nozzle (Sono-Tek) respectively and delivered into the reactors by argon carrier gas with a typical flow rate of 4 l/min. The hot-wall reactor has two heating zones, an evaporation zone and a deposition zone. The former was held at around 130 °C, and the latter was held at around 400 °C. The detailed experimental procedure for the hot-wall process was previously described [5]. An automated syringe pump with a flow rate of 1.5 ml/min was used to transport the precursor solution to the vertical cold-wall reactor, and the substrate temperature was held at about 400 °C. The substrate was typically conventional soda-lime glass, Corning 7059, or commercial moly foils. Fig. 1 shows the schematic of the vertical cold-wall process.

Films were characterized by profilometry (KLA-Tencor HRP 75), X-ray diffraction (XRD) (Philips), scanning electron microscopy (SEM) (Hitachi S-3000N) with energy dispersive spectroscopy (EDS) (EDAX), UV-VIS spectrophotometry (Perkin-Elmer Lamda-19), and a Van der Pauw four point probe system (Bio-Rad HL5500PC).

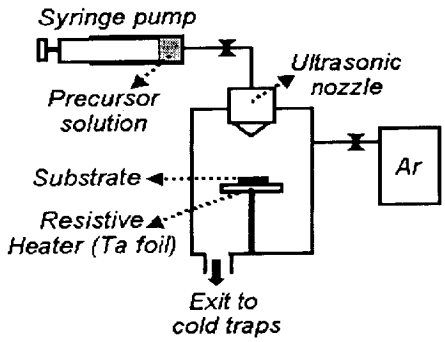

Fig. 1. The schematic of vertical cold-wall process.

RESULTS AND DISCUSSION

Fig. 2 shows representative SEM pictures from the films grown in the both reactors. The film from the hot-wall reactor shows the columnar grain structure with a grain size of about 0.3 μm and the film from the cold-wall reactor shows the granular structure with about same grain size. A previous study reported on the films generated using the same type of the precursor solution also showed that it was possible to deposit micron-thick dense columnar grains with the faceted crystalline features at 400 °C [6]. Columnar grain structure is desirable because it can reduce the areal density of the grain boundary along the current path, which is normal to the film surface in the solar cell materials. Minority carriers generated by photons can recombine at the grain boundary very efficiently reducing the cell efficiency dramatically. If the grain size is, however, sufficiently larger than the film thickness, the recombination at the grain boundary is less important.

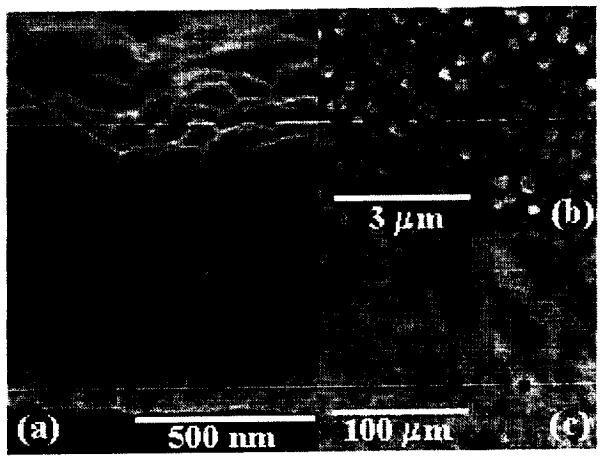

Fig. 2. The images of $CuInS_2$ films deposited by the aerosol process. (a) SEM cross-section image of the film grown in the hot-wall reactor, (b) SEM plane-view image of the film grown in the cold-wall reactor, and (c) optical microscopic image of b with a low magnification.

We ascribe the difference in the grain morphology to film formation at different stages of the aerosol-based thin film deposition [7]. The aerosol containing volatile precursor and solvent may evaporate either partially or completely before it gets to the hot growth surface, and there are three possible pathways for thin film generation. The simplest case is the complete evaporation of the aerosol, which results in the vapor deposition. The process operated under this condition is typically called aerosol-assisted CVD (AACVD). A more complicated case is the incomplete evaporation of the aerosol, followed by the direct contact of liquid droplets at the growth surface and subsequent film formation. This is called (liquid) droplet deposition. The last case is the particle formation above the growth surface and their incorporation into the surface accompanying AACVD or droplet deposition. The particles could be formed either by the precipitation of the solid precursor out of the aerosol or by the decomposition of the precursor followed by the condensation in the gas phase.

The growth of the columnar grain is consistent with AACVD because the film formation is occurring at a molecular level like a conventional CVD process. It is possible to achieve desirable columnar grain growth in the droplet deposition through the careful optimization of the process window. Dense columnar grain growth was experimentally demonstrated by spin-coating [8], which is the most analogous film formation method to droplet deposition. However, it is well known that droplet deposition typically produces porous films with very small grains similar to the granular structure observed in Fig. 2(b). This nano-crystalline grain structure could result from a high nucleation rate through the decomposition of the precursor within each droplet at the hot growth surface.

Growth kinetics at the interface between growth surface and the liquid droplet must be too slow to overcome the decomposition and nucleation rate within the droplet.

Analysis of our films points out the film formation in the hot-wall reactor mainly occurred with AACVD, and the cold-wall reactor was operated with droplet deposition. Accordingly it is reasonable that the zone heating is causing complete evaporation of the aerosol while only partial evaporation occurred in the cold-wall reactor. The latter argument can be further supported by low-magnification plane-view of the film from the cold-wall reactor (Fig. 2(c)) showing the round features possibly created by the liquid phase reaction of the droplets at the growth surface, which was also observed by other workers [9, 10]. Furthermore, the indirect signature for the AACVD can be found in a previous study by Hollingsworth et al. [6], where the same type of hot-wall reactor and precursor were used. The growth rate rarely depended on substrate temperature above 375 °C implying that growth was diffusion limited, and columnar grain growth was clearly observed at 400 °C. It should be noted that dust particles often reported for aerosol processing were also observed in this study. However, dust particles typically followed flow lines above the substrate and only a minimal number of particles were incorporated into the films.

Surface resistance of films was not correlated with grain morphology indicating that majority carrier transport is mainly limited by the density of grain boundaries, in other words, the grain size, which is comparable for both films shown in Fig. 2. Nonetheless, we obtained resistivities ranging from 1 to 30 Ω •cm including the values obtained after post-annealing, which is very promising considering it is comparable to what has been reported for $CuInS_2$ [11] and the lowest resistivity previously achieved with the same type of precursors was between 50 to 100 Ω •cm [12].

The XRD pattern (Fig. 3) obtained from films grown in the cold-wall reactor revealed the typical tetragonal chalcopyrite $CuInS_2$ phase with a (112) preferred orientation including minor phase(s) with the highest intensity at 2θ = 26.3° (marked by '+'), which most likely belongs to a volatile copper sulfide phase. Copper sulfide has a higher band gap than $CuInS_2$ although its conductivity is higher than $CuInS_2$. Post-annealing at 600 °C for 10 min under N_2 flow was very effective removing the secondary phase while it improved the crystalline quality of the $CuInS_2$ phase as shown in Figs. 3 and 4.

For the same film from the cold-wall reactor, the band gap of about 1.46 was approximated from the graph of $(\alpha E)^2$ versus E (Fig. 4), where α is an absorption coefficient estimated from the optical transmittance data and E is photon energy. The steeper band edge upon annealing confirms the improvement of the crystalline quality while the negligible shift in the band gap indicates that the volume percentage of the secondary phase is not considerable even before annealing. It was supported by the phase being nearly stoichiometric with atomic percents for Cu, In, and S as 26 ± 1%, 24 ± 1%, and 50 ± 1%, respectively measured by EDS before annealing. Further evidence is the increase of the electrical conductivity upon annealing because the more conductive phase, copper sulfide was removed by annealing.

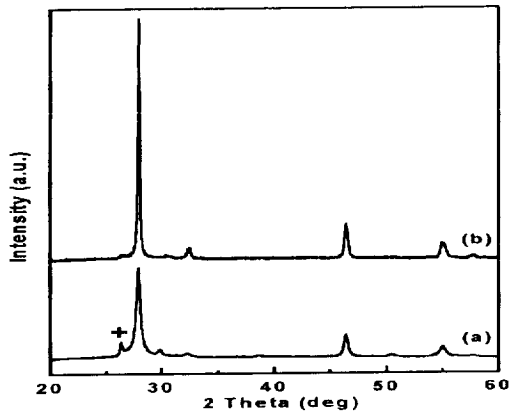

Fig. 3. XRD pattern of the CuInS2 film grown in the cold-wall reactor at 400 °C. (a) as-grown and (b) after annealing at 600 °C for 10 min under N_2 flow.

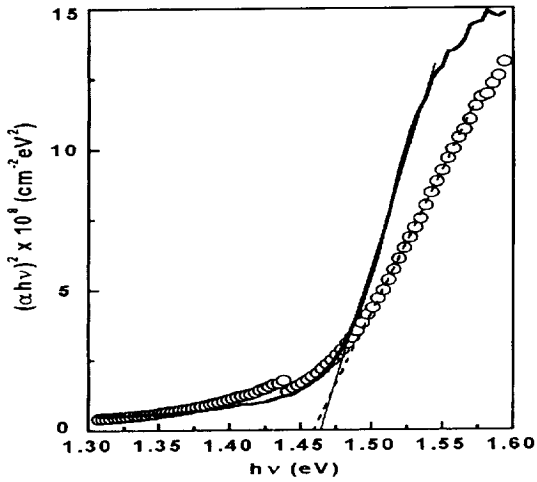

Fig. 4. A plot of $(\alpha E)^2$ versus E for the film grown in the cold-wall reactor at 400 °C; before (open circles) and after annealing at 600 °C for 10 min under N_2 flow (solid line).

CONCLUSION

It is important to understand the complex dynamics of precursor solution evaporation and particle generation during aerosol processing of materials. The film morphology is greatly dependent on the identities of incoming species at the hot growth surface. This study shows two different pathways of aerosol processing. Columnar grain growth with a smooth surface was obtained from AACVD. Granular structure with features related to the liquid phase surface reaction was ascribed to droplet deposition. There was no significant correlation between

morphology and the surface resistivity. It could be attributed to similar grain size and the comparable density of grain boundaries of the films. Nevertheless, it was successfully demonstrated that by using a single-source precursor, stoichiometric polycrystalline $CuInS_2$ thin films with a band gap of approximately 1.45 eV and a resistivity down to 1 Ω •cm after heat treatment, were prepared at a temperature of 400 °C.

Future study will examine fluid dynamics and transport of the aerosol in order to predict the pathway of the aerosol process and to model the behavior of the final form of the precursor solution at the growth surface. This will help us control the process more systematically to obtain a columnar grain structure, which is preferred for solar cell materials because it can minimize the cross section of the minority carrier recombination. The first goal would be to find out the boundary between AACVD and droplet deposition within process parameter space because it is much more feasible to produce the columnar grain structure with the vapor deposition compared to film formation with liquid droplets. It is also necessary to prevent the detrimental solid particle formation in the gas phase reaction.

ACKNOWLEDGEMENT

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